

AD-A101 229

NAVAL RESEARCH LAB WASHINGTON DC
PROPYLENE GLYCOL AS A FIRE SMOKE SIMULANT. (U)

F/6 21/2

JUN 81 M L BORSON, D INDRITZ, H G EATON

NL

UNCLASSIFIED NRL-8477

For 1

403

0 224

END
DATE
FORMED
8-81
DNC

AD A101229

NRL Report 8477

LEVEL II

12
B.S.

Propylene Glycol as a Fire Smoke Simulant

M. L. BOROSON, D. INDRITZ, H. G. EATON, J. P. STONE,
T. T. STREET, J. I. ALEXANDER, AND F. W. WILLIAMS

*Combustion and Fuels Branch
Chemistry Division*

DTIC
ELECTED
S JUL 09 1981 D

June 29, 1981

E



NAVAL RESEARCH LABORATORY
Washington, D.C.

Approved for public release; distribution unlimited.

81 7 10 065

DTIC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER NRL Report-8477	2. GOVT ACCESSION NO. AD-A101 229	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) PROPYLENE GLYCOL AS A FIRE SMOKE SIMULANT.		5. TYPE OF REPORT & PERIOD COVERED Final report on an NRL problem	
7. AUTHOR(s) M.L. Boroson, D. Indritz, H.G. Eaton, J.P. Stone T.T. Street, J.I. Alexander, and F.W. Williams		8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project SO364-SL NRL Problem 61-0070-0-0 NRL Problem 61-0061-0-0	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		12. REPORT DATE June 29, 1981	
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) 11-21-14-1		13. NUMBER OF PAGES 17	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Propylene glycol Training Trainer Toxic gases Smoke			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Attempts are under way to find a safe fire smoke simulant to be used in various types of fire trainers/simulators. Organic aerosol fogs have been suggested as a substitute for real smoke. Stabilized propylene glycol was subjected to thermal and fire stress in ventilated and unventilated chambers. Carbon monoxide produced from the decomposition of the smoke simulant reached 0.8% under some conditions. Chamber temperatures above 66°C (150°F) nearly eliminates the ability to produce smoke.			

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CONTENTS

INTRODUCTION	1
EXPERIMENTAL	1
Aerosol Generator	1
Aerosol Characteristics	2
Small Test Chamber, 0.27 m ³	2
Thermal Stress Experiments	3
Fire Stress Experiments, Part I	5
Gas Analysis	6
Fire Stress Experiments, Part II	7
RESULTS AND DISCUSSION	8
Propylene Glycol Aerosol Characteristics	8
Thermal Stress Results	10
Fire Stress Part I Results	10
Fire Stress Part II Results	11
CONCLUSION	14
ACKNOWLEDGMENTS	14
REFERENCES	14

Accession For	
NTIS GRA&I	
DTIC TAB	
Unannounced <input type="checkbox"/>	
Justification _____	
By _____	
Distribution/ _____	
Availability Codes _____	
Dist	Avail and/or Special
A	

PROPYLENE GLYCOL AS A FIRE SMOKE SIMULANT

INTRODUCTION

In an effort to reduce the hazards associated with training facilities that burn diesel fuel, fire fighting simulators that burn gaseous fuel are under investigation. The use of simulators has many advantages as reported by the Naval Training Equipment Center [1]. Advantages of using simulators include: control of quick start-ups and shut-downs, computer control of extinguishment and reflash rates, nontoxic training environment, nonpolluting burns, and inexpensive training sessions. These simulators, however, require a smoke simulant to be used in conjunction with the gas burners. Hydrocarbon oil fogs have been suggested as obscurants [1]. Propylene glycol (1,2-propanediol), which is considered less toxic than other organics, has also been suggested for smoke simulations requiring high obscuration of vision and low toxicity [1]. The need for the simultaneous use of gas burners and smoke simulants makes investigation of the behavior of propylene glycol in a fire or thermal stress situation necessary. In the work described in this report, propylene glycol aerosol is subjected to thermal and fire stress to determine if: (a) propylene glycol decomposes into toxic products, (b) the lower flammability limit of the aerosol is exceeded, (c) flammable decomposition products are formed, and (d) there are changes in the physical properties of the fog.

The experiments were performed in three different test facilities, a 0.27 m^3 (10 ft^3) pressurizable chamber [2], a 1.8 m^3 (64 ft^3) ventilated chamber, and at the Norfolk, Virginia, Navy Fire Fighting Training Facility, the future site of the Trainer. Table I cites the general goals of the experimental program with the three test facilities.

Table I — Scope of the Propylene Glycol
Smoke Simulation Tests

Pressurizable Chamber	<ul style="list-style-type: none">Under thermal and fire stress of aerosol identify degradation productsFlammability limitsAerosol characterization
Ventilated Chamber	<ul style="list-style-type: none">CO and CO₂ ProductionSmoke density measurementsAerosol characterizationAerosol persistenceOxygen depletion
Navy Trainer	<ul style="list-style-type: none">Aerosol persistenceAerosol mixingAerosol characterization

EXPERIMENTAL

Aerosol Generator

For these tests, two methods were used to create the propylene glycol aerosol: shearing and condensation. To create an aerosol by shearing, a Model III-A aerosol generator was constructed with

Manuscript submitted on February 7, 1981.

improved nozzles [3]. This generator was comprised of two brass cans with two outlets each. The nozzle, having four holes 0.1 cm (0.04 in.) in diameter, was attached to one outlet inside the first can. The other outlet of the first can was attached by a pipe to the first outlet of the second can. The second outlet of the second can was open. Compressed air was directed through the nozzle submerged in propylene glycol. The generated particles then passed through the pipe to the second can where the larger particles deposited. The smaller particles then entered the test chamber.

The second method of aerosol generation, condensation, was accomplished with a Steamaster Company, Inc., Model HPJ-3 electric boiler. This unit was modified by nickel-plating the inside of the boiler to reduce surface catalyzed decomposition of the propylene glycol. The maximum temperature control was raised to operate at 215°C (420°F) and a maximum pressure of 2.76×10^5 Pa (40 psi).

Aerosol Characteristics

To study the behavior of aerosol fogs without thermal or fire stress, tests were carried out at the Fleet Training Center, Norfolk, Virginia. The building measures approximately 10 m × 9 m × 7 m and is divided into four quadrants each two stories high (Fig. 1). All runs were made in quadrant I only, except for run 3 which was made in quadrants I and II. The aerosol generator was located on the first floor just inside an enclosure of three walls with a solid ceiling. Outside the three walls a grating separated the first and second floors. Visual range markers were placed on the second floor and viewed through two portholes. Also, the particle analyzer was located on the second floor. The trainer building is equipped with ventilation louvers near the floor. Union Carbide stabilized propylene glycol (No. 7286-72) aerosol from the Steamaster electric boiler was used as the simulated smoke. The Climet C208 Particle Analyzer was used to measure particle distribution and visual obscuration measurements were made. The aerosol generator was turned on for about 2 min and the aerosol was allowed to diffuse until the room was filled. Visual range measurements were made at 4.3, 3.7, 2.4, 1.8, and 1.2 m by observing the disappearance and reappearance of black numbered index cards.

In order to analyze the mean volume radius produced by the Steamaster electric boiler, the inlet from a Climet C208 Particle Analyzer was attached to the test chamber. Air samples were pumped from the chamber into the analyzer at a rate of 7.08 standard liters per minute (0.25 scfm). The particles pass through the sensor, which is comprised of an elliptical mirror and a high intensity lamp at one focus. As the particles pass in front of the lamp they scatter the light beam. The light is reflected from a mirror and focused on a photomultiplier tube. The scattered light is thus converted to electrical impulses whose amplitude and frequency correspond to size and concentration, respectively. The information from the particle analyzer is then transferred to a multichannel monitor (Climet C210) which counts and groups the particles. The C208 particle analyzer detects particles as small as 0.3 μm in diameter and the C210 multichannel monitor groups them into eight channels (0.3-0.5, 0.5-0.7, 0.7-1, 1-2, 2-3, 3-5, 5-10, and $>10 \mu\text{m}$) and records the number of particles per liter in each channel on magnetic tape.

Small Test Chamber, 0.27 m^3

A portion of the thermal/fire stress experiments was carried out in a 0.27 m^3 stainless steel combustion chamber equipped with three windows for visual observation. The system contained a closed gas sampling loop to provide continuous monitoring of the oxygen, carbon dioxide, and carbon monoxide levels. Complete details of the gas sampling system can be found in Refs. [2,4]. The oxygen is analyzed with a Beckman Instruments, Model F3M3-1AY Oxygen Analyzer with an operating range of 0.0 to 25.0%. The carbon dioxide and carbon monoxide are analyzed with a Beckman Instruments, Model 1R315 Infrared Analyzer with a range of 0.0 to 10.0% and Model 1R315A (some runs with a Model 685) Infrared Analyzer with ranges of 0.0 to 5.0% and 0.0 to 1.0%, respectively. The chamber had outlets through which additional lines could be attached to the chamber. The lines attached included the aerosol outlet, the particle analyzer sample tube, and oxygen, hydrogen, and pro-

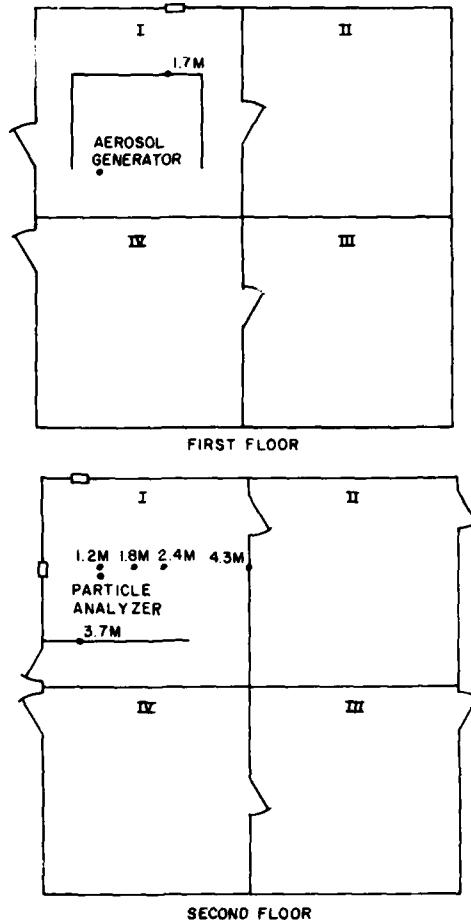


Fig. 1 — Floor plan of the Advanced Firefighting Simulator at Fleet Training Center, Norfolk, Virginia. Numbered cards for visualization tests are shown along with particle analyzer sampling port and aerosol generator location.

pane gas leads. A thermocouple was placed in the flame to monitor its presence in the event the aerosol prevented visual observation.

Thermal Stress Experiments

Thermal stress by nonflaming heating was obtained with a radiant panel heater (heat flux 0.15 W/cm²) controlled with a Variac. The oxygen level remained at 21% for all runs of the thermal stress tests. When the aerosol generator was on, a pressure bleed valve was kept open at the bottom of the chamber to maintain atmospheric pressure.

Three different types of experiments were performed with the aerosol exposed to the radiant panel: two with the shear aerosol generator and one with the condensation aerosol generator. The first experiment (Table 2, test runs 1 and 2) involved keeping the shear aerosol generator on for the entire run. The aerosol was introduced into the chamber for 6 to 12 min to allow an increase in concentration. While the aerosol was still being introduced, the radiant panel was energized. The chamber was batch sampled approximately every 10 min during the run with previously evacuated 1.7-l stainless steel bottles. The heater and aerosol were turned off after a total run time of approximately 60 min.

For the second experiment, the shear aerosol generator was not operated continuously (Table 2, test runs 3 through 7). The aerosol was introduced for 15 to 25 min. The aerosol was then turned off

Table 2 — Thermal Stress Test Using Radiant Panel Heater.
 Aerosol Produced by Shearing Aerosol Generator. (Product
 concentrations are expressed as heptane ($\pm 10\%$)
 equivalent in milligram per cubic meter.)

Contaminants	Test Number									
	1					2				
	Sampling Time, min.									
	10	28	48	60	80	u	10	20	30	60
Methane	0.2	0.4	0.4	0.7	0.8	—	—	0.2	0.4	1.1
Ethylene	0.2	2.1	5.7	7.5	9.3	—	0.1	0.4	1.3	7.3
Propylene	—	—	0.4	0.7	0.9	—	—	—	—	—
Unknown (383)*	—	—	0.1	0.2	0.3	—	—	—	—	0.4
Acetaldehyde	2.4	16	50	77	120	0.6	3.8	11	36	115
Unknown (1107)*	—	—	0.6	0.9	1.4	—	—	—	—	0.6
Unknown (1199)*	—	—	2.3	2.4	6.5	20.0	—	—	—	19.0
Propionaldehyde	1.2	4.2	10	21	27	—	3.1	7.7	20	29
Acetone	—	0.2	0.9	1.1	5.1	—	—	0.3	0.8	5.7
Unknown (1544)*	—	0.2	1.1	1.3	4.0	—	—	0.2	0.6	—
Isobutyraldehyde	—	—	—	0.1	0.6	—	—	—	—	0.4
Unknown (1833)*	—	—	—	0.8	—	—	0.3	—	—	0.2
Crotonaldehyde	0.8	0.7	0.6	0.6	1.1	—	—	0.2	0.2	0.3
Butanol	0.8	0.8	0.3	0.2	0.6	—	0.3	—	—	0.2
Allyl acetate	—	—	0.6	0.9	18	—	—	0.4	0.8	3.5
Unknown (2218)*	14.0	55.0	11.0	60.0	14.0	30.0	32.0	30.0	40.0	40.0
4-Methyl-2-ethyl-1,3-dioxolane	—	—	—	—	4.2	—	—	—	—	0.6
Carbon monoxide**	—	—	0.1	0.2	0.2	—	—	0.1	—	0.1
Carbon dioxide**	0.1	0.1	0.2	0.3	0.4	0.1	0.5	0.1	—	0.2

Contaminants	Testing number							
	3			4		5	6	7
	Sampling Time, min.							
	10	20	30	0	10	20	30	
Methane	0.3	0.3	0.3	0.4	0.4	0.3	0.5	
Ethylene	1.0	0.4	0.9	—	0.3	1.3	3.3	
Propylene	0.1	0.1	0.1	—	—	0.1	0.2	
Acetaldehyde	22	4.8	14	—	4.7	30	71	
Unknown (1097)*	—	—	—	—	—	—	0.2	
Propionaldehyde	8.1	3.2	6.9	—	5.1	20	34.0	
Acetone	0.3	0.1	0.2	0.5	0.1	0.6	4.7	
Unknown (1544)*	0.5	—	0.4	—	0.3	1.9	3.4	
Isobutyraldehyde	—	—	—	—	—	—	0.2	
Unknown (1844)*	—	—	—	—	—	0.2	0.3	
Crotonaldehyde	0.9	0.4	1.1	—	0.9	0.2	0.6	
Butanol	—	—	—	0.5	0.5	0.4	0.3	
Allyl acetate	0.6	—	0.2	—	—	0.6	40.0	
Unknown (2218)*	6.6	31	7.2	—	3.9	21	6.8	
4-Methyl-2-ethyl-1,3-dioxolane	—	—	—	—	—	—	4.5	
Carbon monoxide**	—	—	—	—	—	—	—	
Carbon dioxide**	0.1	0.1	0.1	—	—	0.1	0.1	

*These numbers correspond to gas chromatographic elution times, in hundredths of minutes.

**Carbon monoxide and carbon dioxide concentrations are expressed in percent by volume, respectively.

and the bleed valve closed. Chamber gas samples were collected (as described above) after heating for 0, 10, 20, and 30 min. Additional chamber gas samples, concentrated on a solid adsorbent, Tenax, were subsequently desorbed and analyzed according to a method developed by Eaton [5].

The third experiment utilizing the radiant panel heater was performed with the condensation aerosol generator (Table 3, test runs 1 and 2). The aerosol was introduced into the chamber to achieve the desired level of obscuration. The bleed valve was closed and the heater turned on for approximately 30 min. Batch gas samples were taken either every 10 min or only after the run. Tenax tubes were also used for sample collection for 20 min after each run was completed.

Table 3 — Thermal Stress Test with Radiant Panel Heater and Condensation Aerosol Generator. (Product concentrations are expressed in heptane equivalents ($\pm 10\%$) in milligram per cubic meter.)

Contaminants	Test number				
	1		2		
	Sampling Time, min.				
	0	10	20	30	20
Methane	0.6	0.7	0.8	0.8	2.3
Ethylene	—	0.2	0.3	0.5	1.2
Propylene	—	0.1	0.1	0.2	1.6
Acetaldehyde	2.7	18	28	41	105
Ethanol	—	—	—	0.5	0.7
Propionaldehyde	—	9.6	11	8.4	32
Acetone	—	0.4	0.5	0.9	24
Unknown (1544)*	—	0.1	0.2	0.3	1.1
Isobutyraldehyde	—	—	0.4	—	—
2-Butanone	—	0.1	0.1	—	3.6
Butanol	0.4	0.9	—	0.2	0.3
Allyl acetate	9.3	19	17	11	35
Unknown (2152)*	—	—	—	4.4	—
Unknown (2218)*	13	4	6.5	18	4.5
Crotonaldehyde	—	—	—	—	0.3
4-Methyl-2-ethyl-1,3-dioxolane	—	—	—	—	2.5
Carbon monoxide**	—	—	—	—	—
Carbon dioxide**	0.1	0.1	0.1	0.2	0.1

*These numbers correspond to gas chromatographic elution times, in hundredths of minutes.

**Carbon monoxide and carbon dioxide are expressed in percent by volume, respectively.

Fire Stress Experiments, Part I

Fire stress was applied to the aerosol with a flame from either a hydrogen or propane burner. The oxygen in the 0.27 m^3 chamber air supplied that needed for combustion; therefore, gaseous contaminants in the chamber air were ingested into the burners. The hydrogen flame came from a slot burner and produced a flame (over 2500° K) approximately 2 cm wide \times 6 cm long \times 9 cm high, which in the 0.27 m^3 chamber represents a fire to free space volume ratio of $\sim 0.06\%$. Oxygen was added to maintain the oxygen concentration at 21%. The pressure was kept constant through a bleed valve, originally at the bottom of the chamber and later moved to the top. This modification will be explained later.

With the condensation aerosol generator, the hydrogen torch was lit and the aerosol was turned on and off during the run to maintain the desired obscuration. Batch gas samples were collected, as

described above, after each run (Table 4, test runs 1 through 7). Following the collection of the "whole" gas samples, samples were collected in Tenax tubes for 20 min after each run was completed.

Fire stress applied to the aerosol with the flame from a propane burner (Table 4, test runs 8 and 9), produced a conical flame (over 2000° K) approximately 10.2 cm long and 1.0 cm in diameter at the base (4 in. by 0.75 in.) resulting in a fire to free space volume of ~ 0.01%. Oxygen was maintained at 21% and the bleed valve was kept open at the top of the chamber.

Table 4 — Fire Stress Test—Using Hydrogen Torch or Propane Burner. Aerosol Produced by Condensation Aerosol Generator. (Product concentrations are expressed as heptane equivalents ($\pm 10\%$) in milligram per cubic meter.)

Contaminants	Hydrogen Torch Tests							Propane Burner Tests	
	Run No.							8	9
	1	2	3	4	5	6	7		
Methane	0.3	0.8	23	17	84	2.8	13	4.4	19
Ethylene	0.4	0.9	20	45	108	3.5	15	72	66
Propylene	0.3	1.1	5.8	8.6	16	71	1.6	—	—
Propane	—	—	—	—	—	—	—	1000	550
Allene	0.1	0.1	0.4	1.8	1.5	2.6	—	—	—
Acetaldehyde	8.5	24	27	11	103	26	21	2.9	25
Unknown (705)*	—	—	—	1.6	—	8.7	—	—	—
Isobutane	—	—	—	—	—	—	—	2.7	0.7
Unknown (828)*	—	—	—	—	0.4	—	—	0.2	0.1
Ethanol	—	0.3	3.2	1.8	1.1	1.5	0.9	—	3.5
Unknown (1195)*	—	—	—	—	—	—	—	1.8	—
Propionaldehyde	0.3	1.5	5.4	3.8	7.2	8.7	7.3	—	18
Acetone	0.5	7.4	93	64	80	54	16	0.2	64
Unknown (1450)	—	—	—	—	—	—	0.1	—	0.3
Unknown (1544)	—	—	1.1	3.8	3.2	2.3	3.6	—	3.5
Propanol	—	0.1	3.7	—	1.8	1.9	1.5	—	4.9
Isobutyraldehyde	—	—	—	6.3	—	—	—	—	—
2-Butanone	—	1.0	5.5	3.8	6.2	5.5	1.7	—	4.8
Crotonaldehyde	—	—	0.2	4.4	0.3	0.5	2.2	—	1.2
Butanol	0.7	0.4	—	0.4	1.1	—	0.3	0.4	0.1
Allyl acetate	1.0	14	205	166	190	225	13	—	131
Unknown (2218)*	—	31	34	8	21	40	13	29	34
4-Methyl-1,3-dioxane	—	—	11	3.2	3.6	8.8	3.3	—	42
4-Methyl-2-ethyl-1,3-dioxolane	—	2.0	57	66	35	87	25	—	92
Carbon monoxide**	—	—	0.2	0.6	0.8	0.2	0.3	0.1	0.2
Carbon dioxide**	0.8	0.6	1.3	13	14	11	11	12	11

*These numbers correspond to gas chromatographic retention times, in hundredths of minutes.

**Carbon monoxide and carbon dioxide are expressed in percent by volume, respectively.

Gas Analysis

A Hewlett-Packard Model 5993 gas chromatograph/mass spectrometer (GC/MS) system was used to qualitatively analyze the contaminants collected on the Tenax Sampling tubes. Quantitative measurements with solid adsorbents were not practical under these conditions [6].

The GC/MS system was operated in a continuous scanning mode. The mass spectra obtained were identified by comparison with a mass spectral library with search capabilities and with published compendia of mass spectral data.

Quantitative evaluations were obtained by analyzing the gas samples which were collected in the 1.7-l stainless steel bottles. The analyzer used was a Perkin-Elmer GC, Model Sigma 2, equipped with dual flame ionization detectors and temperature programming. The separation columns used in both the GC and GC/MS analyzers were Porapak Q, 100/120 mesh, 60 cm long by 0.32 cm diameter (2 ft long by 1/8 in. diameter) columns. The column oven was programmed from 50 to 175°C at a rate of 8°/min.

Fire Stress Experiments, Part II

The rate of build-up of carbon monoxide and carbon dioxide in a ventilated space from the interaction of the flame and propylene glycol was determined. Aerosol generated by a modified Steamaster Company, Inc., Model HPJ-3 electric boiler was discharged into a larger chamber producing a 90 to 120 cm (3 to 4 ft) obscuration.

These stress tests were carried out in a 1.8 m³ (64 ft³) chamber equipped with viewing ports for observation of obscuration visually, three variable speed (variac controlled) circulation fans, a variable speed (variac controlled) ventilation fan, a light obscuring device for measuring percent obscuration, and a thermocouple for measuring temperature. For these tests Union Carbide stabilized propylene glycol (no. 7454-25) was used. A schematic of the test chamber is shown in Fig. 2. Samples were continuously withdrawn from the chamber to monitor CO, CO₂, and O₂ levels during the progress of the experiments. The analyzers are the same type as used with the 0.27 m³ chamber. Temperature was also monitored with thermocouples and recorded on a strip chart recorder during the runs.

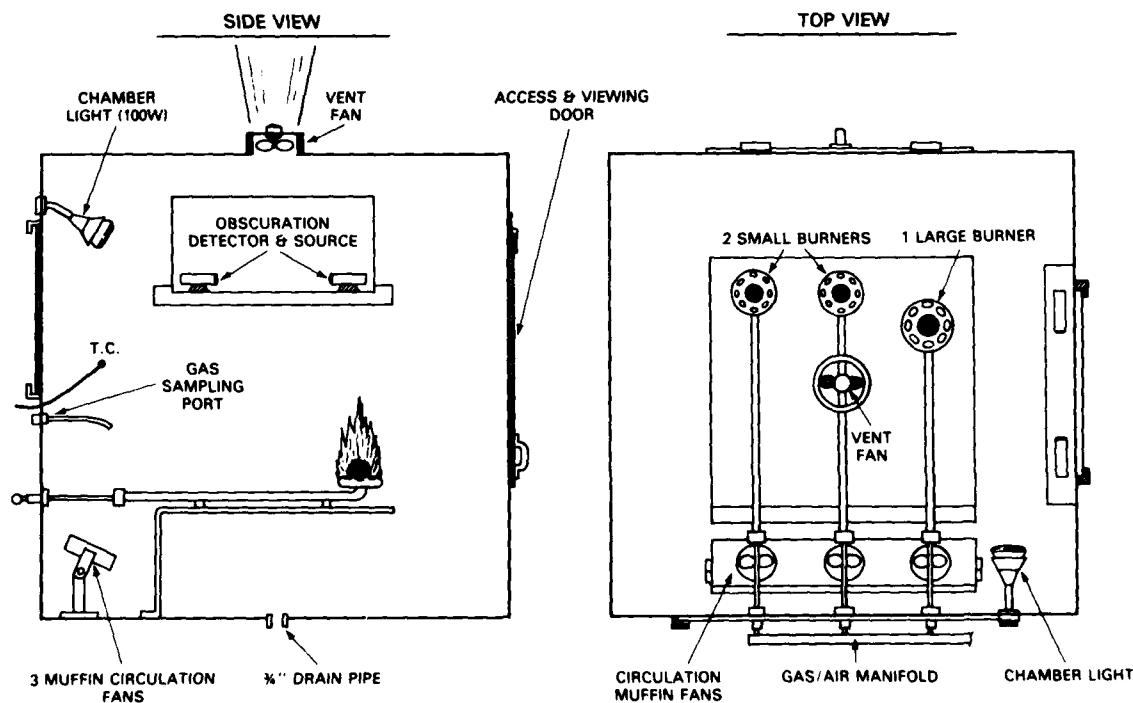


Fig. 2 — Schematic of 1.8 m³ test chamber used to test production of carbon monoxide and carbon dioxide from propylene glycol in a fire environment

Also, additional lines for feeding air and propane to the burners and an aerosol sampling line were attached to the chamber. Air and gas were premixed in a manifold and fed to propane burners. The fuel and air were premixed such that the flame was slightly fuel rich. Thus, the chamber air was not used to maintain the flame and all oxygen consumption can be attributed to the burning of the aerosol. Ventilation flow rates were measured using a Hasting Air Meter, Model AB-27. Ventilation was achieved using a fan mounted at the top center of the chamber exhausting outward. A 1.9 cm (3/4 in.) diameter drain in the bottom plus gaps in the chamber windows supplied the fresh air and maintained constant pressure. The external ventilation supplied 0.5 m³/min (19 ft³/min) air resulting in a total change of air approximately every 3.3 min.

The chamber was constructed in such a way as to facilitate an external measure of visual obscuration. White plates inscribed with large black numbers were added to the inside ceiling at 30-cm intervals.

The experiments were run using one or two propane burners with and without external ventilation. Each of the propane burners produced approximately 1500 cm³ (0.055 ft³) of flame volume. The two burners used were the small burners in Fig. 2. When only one burner was used it was the burner located in the center of the chamber. The fire to free space volume ratio for one and two burner operation is 0.09% and 0.18%, respectively.

RESULTS AND DISCUSSION

Propylene Glycol Aerosol Characteristics

For the aerosol behavior tests conducted in the fire fighting simulator, the sampling line to the particle analyzer was 9 m (30 ft) long, three times the length of the particle sampling tube in all the other experiments described above. A longer sampling tube decreases the total number of particles reaching the analyzer because of absorption on the tube walls. Measurements made with both the long and short sampling tubes indicate up to 20 to 30% of the particles are lost when using the longer tube. The major effect of the adsorption would be the apparent shift of the particle distribution toward smaller particles, since larger particles have a higher frequency for impaction on the wall of the tubing.

The Climet Particle Analyzer was not designed to measure the very high particle concentrations of a heavy fog. Attempts to measure more than 10⁵ particles/s (850 particles/cc) result in a saturation of the particle analyzer even with the long sampling tube. One effect of saturation is coincidence loss, the simultaneous occurrence of more than one particle in the light beam causing a shift in the particle distribution toward the larger particles. The particle analyzer, in this circumstance, would measure a single particle larger than any of the smaller particles simultaneously in the light beam. Coincidence loss of particles in the light beam prevents the observation of the expected particle concentrations of at least 2 × 10⁷ particles/s (200,000 particles/cc) for the degree of obscuration needed.

This saturation shift in measured particle size necessitated the measuring of particles size at low concentrations. These low concentration measurements were used to project the geometric mean particle diameter and the standard deviation (σ) of the diameters. The radius for volume calculation is given by Dinker and Hatch [7] as radius = $(\log_{10}^{-1} (\log_{10} (\text{mean particle diameter}) + 3.4539 \log_{10}^2(\sigma))) / 2$. Because the saturation effects limited the accuracy of total particle counts, the aerosol density was calculated by a method based on visual range and particle size from the equations given by Davies [8]. This treatment utilizes the equation

$$M = \frac{5.2 r P}{VE} .$$

where

M = aerosol density (in g/m^3),

r = mean volume radius (in μm),

V = visual range (in m),

E = extinction coefficient,

and

ρ = density of liquid (g/ml).

Table 5 presents a typical data set for variation of visual range, density, and particles per cubic centimeter with respect to time for the tests run in the Norfolk Fire Fighting Training Simulator. Visual range measurements were made from 1.2 to 4.3 meters for all runs. The aerosol density ranged between 0.53 and $1.8 \text{ g}/\text{m}^3$ and the total number of particles/cc, calculated from the density and from the mean particle diameter of $1.5 \mu\text{m}$, varied from 0.3×10^7 to 1.0×10^7 .

Table 5 — Aerosol Behavior Test
Without Thermal or Fire Stress. Aerosol Produced
by Condensation Aerosol Generator.

Time (min)	Mean Volume Radius (μm)	Visibility (m)	Density (g/m^3)	Particles/cc $\times 10^6$ (cm^{-3})
1.28	0.75	4.3	0.52	0.29
1.43	0.75	3.7	0.61	0.34
2.27	0.75	2.4	0.92	0.50
2.55	0.75	1.8	1.23	0.67
2.83	0.75	1.2	1.84	1.00
4.40	0.75	1.2	1.84	1.00
5.80	0.75	1.8	1.23	0.67
6.80	0.75	2.4	0.92	0.50
8.07	0.75	3.7	0.61	0.34
8.63	0.75	4.3	0.53	0.29

Conditions for the various runs in the fire training simulator were not constant. Differences in wind velocity significantly altered the aerosol persistence for the tests because of the louvers at the bottom of the test building's walls. Table 6 shows the data for runs 1 through 4 which were conducted on a single day with very strong winds which decreased throughout the day. In run 3, however, the effect of doubling the room size (opening hatches to quadrant II) dominated the decreasing wind velocity. As would be expected, the aerosol persistence was inversely proportional to wind velocity, and room size. To study the effects of wind velocity and room size, the relationship between visual range and time was divided into three parts: (i) decay (visual range decreasing $4.3 \rightarrow 1.2$ meters), (ii) saturation (visual range staying 1.2 meters or less), and (iii) increase (visual range increasing $1.2 \rightarrow 4.3$ meters).

The half-life of visual range during decay was calculated for each run. This half-life is the time necessary for the visual range to decrease to one half of its original value. Table 6 shows some typic-

**Table 6 — Persistence Times for Build up,
Saturation, and Decay of Aerosol**

Run	Decay Half-life Visibility (s)	Saturation Times (s)	Build up Half-life of Visibility (s)
1	57	94	139
2	48	169	156
3	36	68	109
4	55	248	210

half-lives for the decay of visual range. The decay curves seem independent of both wind velocity and room size. In fact, the fastest decay occurs in run 3, in which two rooms were involved. Differences in the decay curves therefore seem mainly dependent on the temperature, pressure, and flow rate of the aerosol generator (and not the ventilation and room size).

The saturation time of the visual range-time plot was based on the shortest distance (1.2 m) measured during the runs. The times of disappearance and reappearance of the 1.2-m marker were recorded (Table 6). A significant increase in the persistence of the aerosol to maintain less than 1.2-m visual range occurred as the wind velocity decreased. The large drop in persistence in run 3 was expected since the room size was doubled.

The increased range portion of the visual range-time plots followed the same pattern as the saturation times. The half-lives for the four runs increased significantly as the winds decreased, except in run 3 when the half-life dropped to the lowest of the four runs because of the increased room size. From the increasing half-lives, the corresponding saturation time, the relative wind velocity, and the room size, the time that visual range is less than a designated distance can be estimated with fairly good accuracy. This ability to estimate the persistence of the aerosol fog can be used in designing the trainer and the length of training tests to be used.

Thermal Stress Results

The concentration and number of contaminants evolved from the thermal stress tests of propylene glycol using either the shearing aerosol generator, Table 2, or the condensation generator, Table 3, appear to be much the same. In each case, production of partially oxidized or pyrolyzed products is directly related to the length of the heating period. However, carbon monoxide (CO) and carbon dioxide (CO₂) do not appear to correlate with heating time.

The major organic products detected in these experiments were: acetaldehyde, propionaldehyde, acetone, allyl acetate, and an unidentified compound, 2218.

No major changes in the physical appearance of the propylene glycol fog were noted under thermal stress. The persistence was not affected and no indication of ignition was observed.

Fire Stress Part I Results—(Experiments carried out in the 0.27 m³ combustion chamber)

As discussed above, this test was conducted by introducing propylene glycol and oxygen during the run in addition to the amount of aerosol needed to initially obscure the chamber. Thus, the results obtained in Table 4 were influenced by the amount of aerosol used, time the burner was on, concentration of oxygen (O₂) throughout the run, and the times that the samples were withdrawn from the test chamber.

In spite of attempts to maintain the O₂ concentration at 21% throughout the experiment, this value dropped in some cases at the end of the tests.

The major organic products detected from these experiments were: methane, ethylene, propylene, acetaldehyde, acetone, allyl acetate, 4-methyl-2-ethyl-1, 3-dioxolane, and an unidentified material, 2218. The major products were the same for the hydrogen and propane burners.

In both fire stress experiments, carbon monoxide (CO) was produced. With the hydrogen torch and the condensation aerosol generator, the CO concentration ranged from 0.1% to 0.8%. Runs made with the propane torch produced a CO concentration up to 0.2%. Although the increase is not linear, the higher production rate of CO for the hydrogen flame may be explained by the larger flame volumes. Fire volume to chamber volume ratios are used only to indicate relative flame sizes.

The hotter and larger flame, hydrogen, caused a heat buildup in the chamber which in turn caused severe aerosol stratification. Runs made with the hydrogen torch caused almost immediate layering with the aerosol being confined to the bottom of the chamber while runs made with the smaller propane flame did not cause layering. This layering effect was the reason the pressure relief vent was moved from the bottom of the chamber to the top. In this way gases were vented instead of the aerosol. The layering effect exhibits a limitation since this action does not simulate smoke, which would rise. The aerosol, unlike smoke, is warm but not hot and therefore not buoyant. Efforts to observe whether the propane flame could cause layering as the chamber air grew hot were prevented by other phenomena: a pressure wave, the ignition of the aerosol vapor and the burning of the hot liquid condensate.

Aerosol ignition takes place with both the hydrogen torch and the propane burner. Ignition appears to occur only when the flame is actually impinging upon the generated aerosol. Hydrogen runs lasted longer probably because of the immediate layering of the aerosol. When efforts to maintain the aerosol obscuration level forced the aerosol layer up to the flame, the aerosol system ignited. For the propane runs, aerosol ignition occurred within 1 or 2 min after turning on the aerosol. With the propane flame, the aerosol is distributed more evenly throughout the chamber. Ignition seems to occur in localized areas then spreads throughout the chamber. The flame front bridges the 60-cm (2 ft) gap across the chamber to the condensate pool, igniting the liquid there formed by condensation of propylene glycol at the end of the aerosol outlet. This pool burns persistently until extinguished or consumed. Some of the hot liquid propylene glycol was collected from the aerosol outlet and subjected to a flash point test. Its flash point was 26°C below the flash point of new propylene glycol, 99°C [9]. Small amounts of decomposition products in the propylene glycol can greatly reduce its flash point [10].

In some instances a pressure pulse moves through the chamber and extinguishes the hydrogen or propane flame. In these instances the pool fire had not been initiated. A pressure transducer on the chamber records a pressure of over 2 atmospheres but the transducer is not designed to respond to fast pressure changes. Thus, the actual peak pressure is undoubtedly higher. It is not clear what the mechanism of the explosion or ensuing fire is and further experiments will have to be performed to understand this potential hazard.

Fire Stress Part II Results—(Results of the experiments carried out in the 1.8 m³ (64 ft³) chamber, Fig. 2)

The average time to maximum CO₂ level during the run was approximately 7.5 min. The temperature rise within the chamber during the runs depended on the number of burners used and whether ventilation was provided. Since the chamber air volume was totally changed every 3.3 min through ventilation, it was not possible to stabilize the temperature within the chamber. Vaporization characteristics of the propylene glycol with respect to temperature made it impossible to maintain 0.9 to 1.2 m (3 to 4 ft) obscuration levels when the chamber temperature exceeded 60°C (140°F). Attempts to produce the

BOROSON, INDRITZ, EATON, STONE, STREET, ALEXANDER, AND WILLIAMS

desired obscuration levels in the chamber when its air temperature exceeds 60°C (140°F) will produce more vapors than condensate. This condition lends itself to the possibility of a rapid build-up of propylene glycol vapor which would result in an explosion.

The 0.9 to 1.2 m (3 to 4 ft) obscuration levels were easily obtainable with one burner when external ventilation was used, but more difficult if there were no external ventilation or if more than one burner were involved at a time. Some of the stabilized propylene glycol (No. 7454-25) was collected and subjected to a flash point test. Its flash point was 4°C below the flash point, 105°C, of new stabilized propylene glycol. Results of the CO, CO₂, O₂ and temperature produced in the matrix of runs are summarized in Table 7 and Figs. 3 and 4.

Table 7 — Ventilated Chamber Test Results—Production
of Carbon Monoxide and Carbon Derived from Fire Exposure to
Propylene Glycol

Type of Experiment	Run No.	Gas Concentrations			Temperature of		Time to MAX CO min
		CO ppm	CO ₂ %	O ₂ %	MIN °F*	MAX °F	
I One Burner, Ventilated	A	250	0.45	—	—	—	12.0
	B	200	0.7	19.85		155	5.5
	C	100	0.25	20.6	100	141	6.0
	D	270	1.0	19.8	145	165	6.0
II Two Burner, Ventilated	A	750	2.5	—	—	—	6.0
	B	600	2.1	18.5	110	254	1.0
	C	1000	1.9	18.0	168	238	5.0
	D	1700	2.5	13.0	160	310	5.0
III One Burner, Unventilated	A	700	8.2	—	—	—	17.0
	B	450	5.0	—	—	—	10.0
	C	375	5.0	—	—	—	11.3
	D	900	4.5	—	—	—	11.0
	E	300	2.3	18.3	90	145	7.5
	F	100	2.0	18.2	110	154	8.0
	G	75	3.0	18.0	90	145	7.5
	H	1150	4.0	16.5	147	212	6.0
	I	775	3.9	15.3	128	172	9.0
IV Two Burner Unventilated	A	3000	4.2	—	—	—	9.5
V Background Test No. Propylene Glycol	Vented one burner	0.0	0.2	20.0	124	134	6.0
	Vented two burners	100	1.4	19.4	110	182	8.0
	Unvented one burner	—	3.8	—	—	—	8.0

*Temperature of chamber when propylene glycol was introduced.

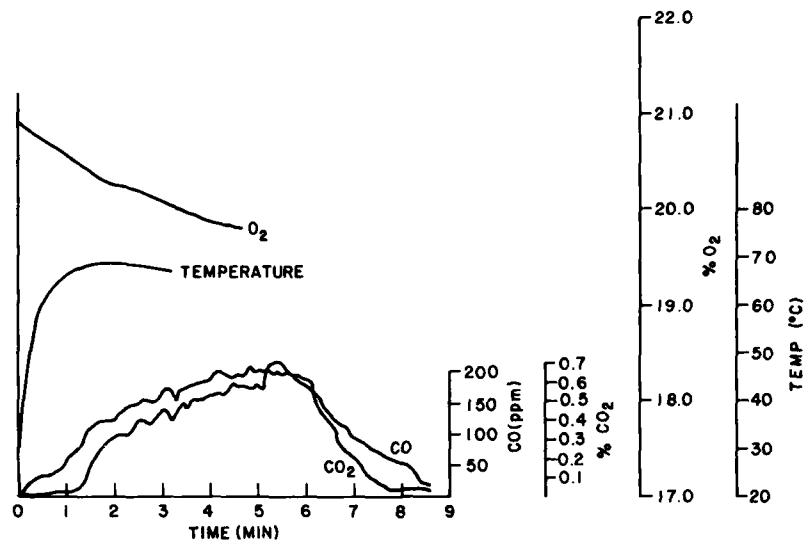


Fig. 3 — Production of carbon monoxide and dioxide with ventilation and one burner in 1.8 m³ chamber. This corresponds to type IB experiment in Table 7.

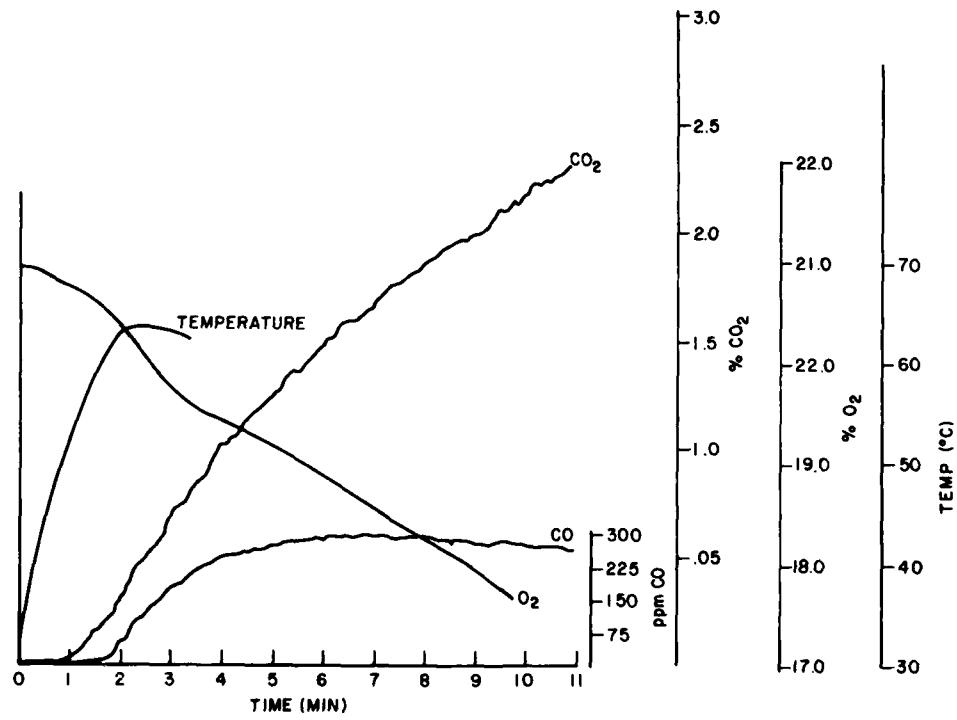


Fig. 4 — Production of carbon monoxide and carbon dioxide without ventilation and one burner in 1.8 m³ chamber. This corresponds to Type III E experiment in Table 7.

CONCLUSION

A smoke simulant is desired that is nontoxic, persistent, and nonflammable. However, from the experiments conducted, these criteria were not met by propylene glycol in the presence of a flame or radiant heat in the 0.27 and 1.81 m³ test chambers. Toxic amounts of CO were produced with the radiant heater and by a propane flame with only a 0.01% fire volume ratio in a 0.27 m³ chamber. Although the amount of CO does not increase linearly with fire volume ratio, greater amounts of CO should be expected from larger flames. The aerosol is persistent in only very small flames (approximately 0.01% fire volume ratio). Otherwise the rate of heat release causes severe layering and smoke is not simulated. Layering might be prevented by ventilation and circulation inside the trainer despite the much larger flames; however, in the fire tests with the propane torch in the pressurizable chamber, explosions occurred in the absence of layering. If temperatures exceed 60 to 66°C (140 to 150°F), vast amounts of propylene glycol vapor are produced, increasing the chances of an explosion unless the amount of propylene glycol in the aerosol generator is limited. For instance, in the 0.27 m³ (10 ft³) chamber with no ventilation, 21 grams of vaporized aerosol would exceed the lower flammability limit. However, in a trainer of 270 m³, 21 kilograms of liquid propylene glycol would be needed to exceed the lower flammability limit assuming complete mixing. Because of high CO concentrations generated from the decomposition of the aerosol, a self-contained breathing apparatus would have to be worn by all personnel in the area of the smoke simulation. Methods of avoiding propylene glycol vapor build-up by maintaining temperatures below 60-66°C would have to be used. If problems of layering and ignition of hot propylene glycol cannot be prevented in a full scale trainer, propylene glycol cannot be used as a smoke simulant in the presence of a flame.

ACKNOWLEDGMENTS

This work was funded in part by NTEC, Orlando, Fla. and NAVMAT. The authors would like to thank Mr. Edward Swiatosz from NTEC for his many helpful discussions and active interest in the program. We would also like to thank the personnel at the Navy Fire Fighting Training School, Norfolk, Virginia, for their assistance in conducting the full-scale tests at their facilities.

REFERENCES

1. E. Swiatosz and P. Grimmer, "Experimental Research For Advanced Firefighting Simulators," Technical Report: NAVTRAECUIPCEN IH-303, May 1978.
2. P.A. Tatem, R.G. Gann and H.W. Carhart, "Pressurization with Nitrogen as an Extinguishment for Fires in Confined Spaces," Combustion Science and Technology, 7, 213 (1973).
3. W.H. Echols and J.A. Young, "Studies of Portable Air-Operated Aerosol Generators," NRL Report 5929, July 1963.
4. P.A. Tatem and F.W. Williams, "The Degradation Products from a Polyaramide Under Low and High Temperature Stresses," J. of Combustion Toxicology, 6, 258 (1979).
5. H.G. Eaton, "A Gradient Heat Desorption Technique of Preconcentrated Tenax GC Tubes for Use in GC/MS Analysis," J. of Chromatog. Sci., 18, 580 (1980).
6. H.G. Eaton, P.A. Tatem and F.W. Williams, "Combustion Products Evaluation from Insulation Materials Coated with Fire Retardant Paints," NRL Report 8403, August 1980.
7. Drinker and Hatch, *Industrial Dust*, McGraw-Hill, New York, p. 147, 1936.

NRL REPORT 8477

8. C.S. Davies, "Visual Range and Size of Atmosphere Particles," *J. Aerosol Science*, Vol. 6, pp. 335-347, 1975.
9. National Fire Protection Association Manual 325 M, Boston, Mass.
10. W.A. Affens and G.W. McLaren, "Flammability Properties of Hydrocarbon Solutions in Air," *J. Chem. and Eng. Data*, 17, 482 (1972).